<Division of Multidisciplinary Chemistry> Molecular Rheology

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- Molecular Rheology -

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Prof CHHABRA, Raj P. Indian Institute of Technology, 6 July 2004

Scope of Research

The molecular origin of various rheological properties of material is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluid while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.

Research Activities (Year 2004)

Presentations

Detailed Investigation of Entanglement Dynamics with Dielectric and Viscoelastic Methods, Watanabe H, Microsymposium on Polymer Melt Rheology and Processing, Yonezawa, 17 - 18 March.

Detailed Investigation of Entanglement Dynamics with Dielectric and Viscoelastic Methods, Watanabe H, Annual APS March Meeting, Montreal, Canada, 22 - 26 March.

Nonlinear Rheology of Detergent Solutions, Inoue T, Annual Meeting of the Society of Rheology Japan, Tokyo, 13 - 14 May.

Dynamic and Viscoelastic Study of Entanglement Dynamics, Watanabe H, II International Conference on Times of Polymers, Ischia, Italy, 20 - 23 June.

Nonlinear Rheology of Multiarm Star Chain and Related Soft Materials, Watanabe H, HUSC Conference - Colloids and Polymeric assemblies near to and far from equilibrium -, Crete, Greece, 25 - 27 June.

Dielectric and Viscoelastic Investigation of Entanglement Dynamics, Watanabe H, Polymer Physics Gordon Conference, New London, USA, 1 - 6 August.

Viscoelastic and dielectric behavior of entangled blends of linear polyisoprenes: test of tube dilation picture, Watanabe H, The XIVth International Congress on Rheology, Seoul, Korea, 22 - 27 August.

Nonlinear rheology of aqueous detergent solutions, Inoue T, XIVth International Congress on Rheology, Seoul, Korea, 22 - 27 August.

Rheo-dielectric behavior of poly(ethylene oxide) containing lithium perchlorate, Matsumiya Y, The XIVth International Congress on Rheology, Seoul, Korea, 22 - 27 August.

Rheology of living bifunctional polybutadienyl dilithium chains in benzene: viscoelastic evaluation of aggregate lifetime, Oishi Y, The XIVth International Congress on Rheology, Seoul, Korea, 22 - 27 August.

Electric Birefringence of Poly(Propylene Glycol), Kikuchi T, the Discussion Meeting of the Society of Rheology Japan, Hirosaki, 22 - 24 September.

Dielectric Relaxation and Rheology of Lithium Per-

Orientational Anisotropy for Rouse Eigenmodes during Creep and Recovery Processes

The Rouse model is a fundamental molecular model for polymer dynamics and its dynamic behavior under step strain has been fully analyzed in literature [1]. However, surprisingly, no analysis has been made for the orientational anisotropy of the Rouse eigenmodes during the creep and recovery processes. For completeness of the analysis of the model, this anisotropy is calculated from the Rouse equation of motion [2].

The calculation, conducted with the Laplace inversion method on the basis of the pole analysis, is simple and straightforward. However, the result is intriguing in a sense that the anisotropy amplitudes A_p of the Rouse eigenmodes during the creep/recovery processes are mutually correlated with each other because of the constant stress requirement. For A_p of the higher order eigenmodes with $p \geq 2$, this correlation results in prominent overshoot and undershoot (to negative values) during the creep and recovery processes, respectively (see Figure 1.). Correspondingly, each Rouse eigenmode has a distribution in the retardation time. These features are quite different from those under strain-controlled relaxation/flow processes where each eigenmode is associated with a single characteristic time and thus the modes behave independently to have monotonically growing/decaying anisotropy amplitudes.

1. H. Watanabe, *Prog. Polym. Sci.,* 24*(9),* 1253-1403 (1999).
2. H. Watanabe and T. Inoue, *Rheol. Acta,* 43*,* 634-644 (2004).

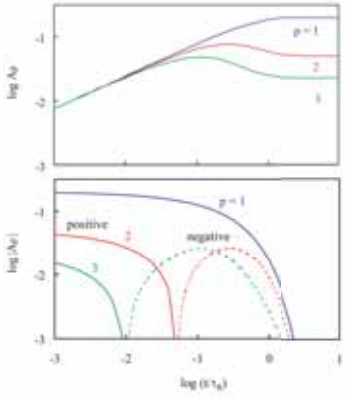

Figure 1. Evolution of anisotropies of Rouse eigenmodes during creep (top panel) and recovery (bottom panel). The anisotropy amplitudes are plotted against normalized time, t/τ_R (τ_R = Rouse relaxation time).

Linear Viscoelastic Behavior of Perfluorooctyl Sulfonate Micelles: Role of Cations

Rheological behavior of threadlike micelles of anionic surfactants has been a subject of extensive research [1]. Nevertheless, the role of counter cation in this behavior has not been fully elucidated. This role was examined for a series of aqueous solutions of perfluorooctyl sulfonate ($C_8F_{17}SO_3^-$; FOS) micelles having a mixture of tetraethylammonium ($N^+(C_2H_5)_4$; TEA) and tetramethylammonium ($N^+(CH_3)_4$; TMA) ions as the counter cations [2]. The solutions had the same FOS concentration (0.045 mol L^{-1}) and various TEA fraction in the counter cations, $\phi_{TEA} = 0 - 1$, and the spherical FOS micelles therein were connected into threads and further organized into dendritic networks.

For $\phi_{TEA} \geq 0.5$, the FOS threads/networks exhibited the Maxwell-type terminal relaxation reflecting their thermal scission. In this range of ϕ_{TEA}, the terminal relaxation time τ drastically increased with decreasing ϕ_{TEA} (see Figure 2.). On a further decrease of ϕ_{TEA} below 0.3, τ became insensitive to ϕ_{TEA} possibly because the motion of the threads *in the unscissored form* became faster than the thermal scission to govern the terminal relaxation.

These rheological features reflected the effects of TEA and TMA on the thermal scission of the FOS threads/networks: Since the charge was the same for TEA and TMA but the bare radius was smaller for TMA, the TMA cations should be preferentially bound on the FOS thread. The thermal scission of the FOS thread, occurring through an exchange of the bound and non-bound TEA cations [3], appeared to be strongly suppressed by the preferentially bound TMA cations that effectively blocked the exchanging sites. Indeed, in a range of $\phi_{TEA} \geq 0.5$ where the thermal scission governed the relaxation of the system, the rheological data were well described by a simple model considering this blocking effect (solid curve in Figure).

1. H. Hoffmann and J. Würtz, *J Molecular Liq,* 72, 191 (1997).
2. H. Watanabe and T. Mori, *J. Soc. Rheol. Japan,* 32, 155-160 (2004).
3. H. Watanabe, T. Sato, K. Osaki, M. Matsumoto, D. P. Bossev, C. E. McNamee, and M. Nakahara, *Rheol. Acta,* 39, 110 (2000).

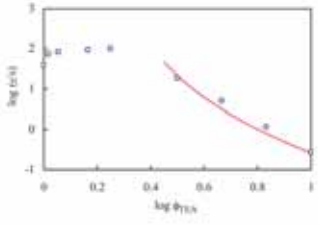

Figure 2. Dependence of terminal relaxation time of threadlike FOS micelles at 20°C on the TEA fraction in the counter cations.

chlirate/Poly(Ethylene Oxide) System, Matsumiya Y, the Discussion Meeting of the Society of Rheology Japan, Hirosaki, 22 - 24 September.

Partial Tube Dilation in Entangled Binary Blends, Watanabe H, the Discussion Meeting of the Society of Rheology Japan, Hirosaki, 22 - 24 September.